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## LATTICE DYNAMICS OF TETRACYANOETHYLENE

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Lattice dynamics calculations for both crystalline forms of tetracyanoethylene are presented. The comparison of the calculated static and dynamical properties with the experimental data, leads us to suggest an improved parameter set for the "6-exp" potential function for crystals with cyano groups.

### 1. Introduction

Tetracyanoethylene (TCNE), one of the most common acceptors in EDA complexes, forms two crystalline modifications: monoclinic [1], stable above 292 K, and cubic [2], stable below this temperature. The study of the lattice dynamics of the crystal is interesting and important from the following reasons. Because of the phase transition near room temperature it is possible to obtain rather large single crystals of both crystalline phases and perform more or less complete studies by Raman [3] and Brillouin [4] scattering, far-infrared reflection [4] and possibly inelastic neutron scattering [5]. The fact that there are only two centrosymmetric molecules in the monoclinic unit cell and three in the primitive cubic cell is a great advantage for all experimental methods and the fact that all atoms in the TCNE molecule are good inelastic neutron scatterers makes an additional advantage for the latter method. Furthermore, the complete experimental results together with some theoretical work will form a good base for the interpretation and understanding of the phase transition. We start with the easiest but rather important part of the work — lattice dynamics calcu-

lations within the harmonic approximation. The aim of this work is to establish a semi-empirical potential function for the TCNE crystal (discussing the transferability of the potential for different crystalline phases) partly as a preparation for self-consistent phonon calculations which we plan to do in the future.

### 2. Results of structure and dynamics calculations

There is only one paper [6] about an atom—atom potential function for crystals with cyano groups and the paper is concerned with a simple "6-exp" function. On the other hand, the derivation of a new complete intermolecular potential for TCNE molecules by using ab initio calculations as, for example, for ethylene [7], will be not so easy. Only for the long range  $r^{-6}$  interactions carbon and nitrogen parameters have recently become available from ab initio calculations on azabenzenes [8]. Therefore, we decided to start with the empirical "6-exp" potential and parameters suggested by Govers [6], but also to check the ab initio calculated  $r^{-6}$  parameter set. The standard lattice dynamics calculations, based on the description given by Pawley [9] (within the harmonic and rigid-body approximations) with preliminary structure minimization were performed. The structure was optimized with respect to

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the lattice energy using the program package MINUIT [10] in two series of steps with SIMPLEX and MIGRAD procedures, respectively. The lattice sum was taken over 42 neighbouring molecules, after checking that the inclusion of further shells did not influence the results anymore.

### 2.1. The monoclinic form

The monoclinic modification of TCNE crystallizes with the space group  $P2_1/n$  and two centrosymmetric molecules in the unit cell [1] (parameters of the cell are given in table 1). As it can be seen from this table, the "6-exp" potential with the parameters suggested by Govers [6] gave results far from satisfactory, in spite of the fact that these parameters were derived from structural properties for a few crystals with cyano groups (including monoclinic TCNE). One could expect that the introduction of the electrostatic

interactions via the "6-exp-1" function should improve the results. However, the results of calculations presented in the next column of table 1 with Govers' parameters and atomic net charges taken from ref. [2]) show that the reproduction of the experimental static and dynamic properties of the monoclinic TCNE is even worse. Of course, one can suggest to vary the net atomic charges but this would mean that the Coulomb term simply adds more adjustable parameters rather than new physical insight, similarly to what has been concluded in the case of *p*-dichlorobenzene [11]. In fact every semi-empirical improvement of the "6-exp" function can be interpreted this way. Moreover, it is not justified to add the electrostatic term to the "6-exp" potential which was optimized without this term.

So, in order to limit the number of adjustable parameters we decided to use the simple "6-exp" function, keeping the parameters  $A_i$  (dispersion interactions) and the pre-exponential factors,  $B_i$  as given by

Table 1  
Comparison of the experimental and calculated static and dynamical properties for the monoclinic TCNE

Properties		Calculations				Experimental values
		"6-exp" $C = 3.60 \text{ \AA}^{-1}$ [6]	"6-exp-1"	"6-exp" $C = 3.46 \text{ \AA}^{-1}$ [8]	"6-exp" $C = 3.46 \text{ \AA}^{-1}$	
lattice constants a)	<i>a</i>	6.93	6.60	7.34	7.44	$7.51 \pm 0.075 \text{ \AA}$
	<i>b</i>	6.08	6.01	6.54	6.50	$6.21 \pm 0.062 \text{ \AA}$
	<i>c</i>	6.68	6.56	6.98	7.01	$7.00 \pm 0.070 \text{ \AA}$
	$\beta$	$105.26^\circ$	$106.67^\circ$	$107.69^\circ$	$104.32^\circ$	$97.16 \pm 0.1^\circ$
Euler angles a, c)	$\mu$	$-6.03^\circ$	$-4.82^\circ$	$-3.85^\circ$	$-5.53^\circ$	$-8.85^\circ \pm 1.0^\circ$
	$\psi$	$-23.97^\circ$	$-25.08^\circ$	$-25.49^\circ$	$-22.61^\circ$	$-17.60^\circ \pm 1.0^\circ$
	$\theta$	$-27.91^\circ$	$-29.90^\circ$	$-29.50^\circ$	$-28.36^\circ$	$-28.18^\circ \pm 1.0^\circ$
lattice energy (kcal/mole)		-17.22	-34.19	-12.53	-11.00	
librational frequencies b)	$A_g$	78.2	89.2	54.0	54.8	$65 \pm 2$
	$A_g$	98.2	152.6	81.1	77.5	$76 \pm 2$
	$A_g$	129.8	174.6	103.2	100.8	$100 \pm 2$
	$B_g$	38.3	52.7	36.3	29.1	$29 \pm 2$
	$B_g$	119.5	115.8	102.4	91.8	$89 \pm 2$
	$B_g$	135.7	149.9	112.5	105.7	$112 \pm 2$
translational frequencies (cm <sup>-1</sup> )	$A_u$	42.8	74.6	31.5	25.3	—
	$A_u$	116.7	162.7	99.7	89.4	—
	$B_u$	98.8	146.6	84.5	73.3	—

a) Experimental values according to ref. [11].

b) Detailed experimental work on Raman scattering will be published [3].

c) For the definition of the Euler angles see ref. [7].



Govers and to fit the exponent  $C$  (assuming the latter to be equal for all C...C, C...N and N...N contacts) for the best agreement with experimental data. For the dispersion parameters  $A_i$ , Govers' values are supported by their reproduction [8] of the ab initio calculated dispersion interactions in azabenzenes. To determine the best value of the parameter  $C$ , the minimum value of  $\chi^2$ , defined as the sum of the squares of the differences between observed and calculated structure parameters as well as librational frequencies at the cone centre, was sought. In fact  $\chi^2$  was a weighted sum as we fitted a wide variety of data and we used the weights suggested by Starr and Williams [12]. Fig. 1 shows the variation of  $\chi^2$  with the parameter  $C$ ; the minimum of the function  $\chi^2$  indicates an optimum  $C$ -value of  $3.46 \text{ \AA}^{-1}$ . It is interesting to note that the function  $\chi^2$  calculated for structural parameters only, has a very broad minimum; in fact the comparison with librational frequencies determines the optimum value for the parameter  $C$ . The results of the calculations for  $C = 3.46 \text{ \AA}^{-1}$  are presented in table 1, together with the results for a parameter set with the  $A$ -val-

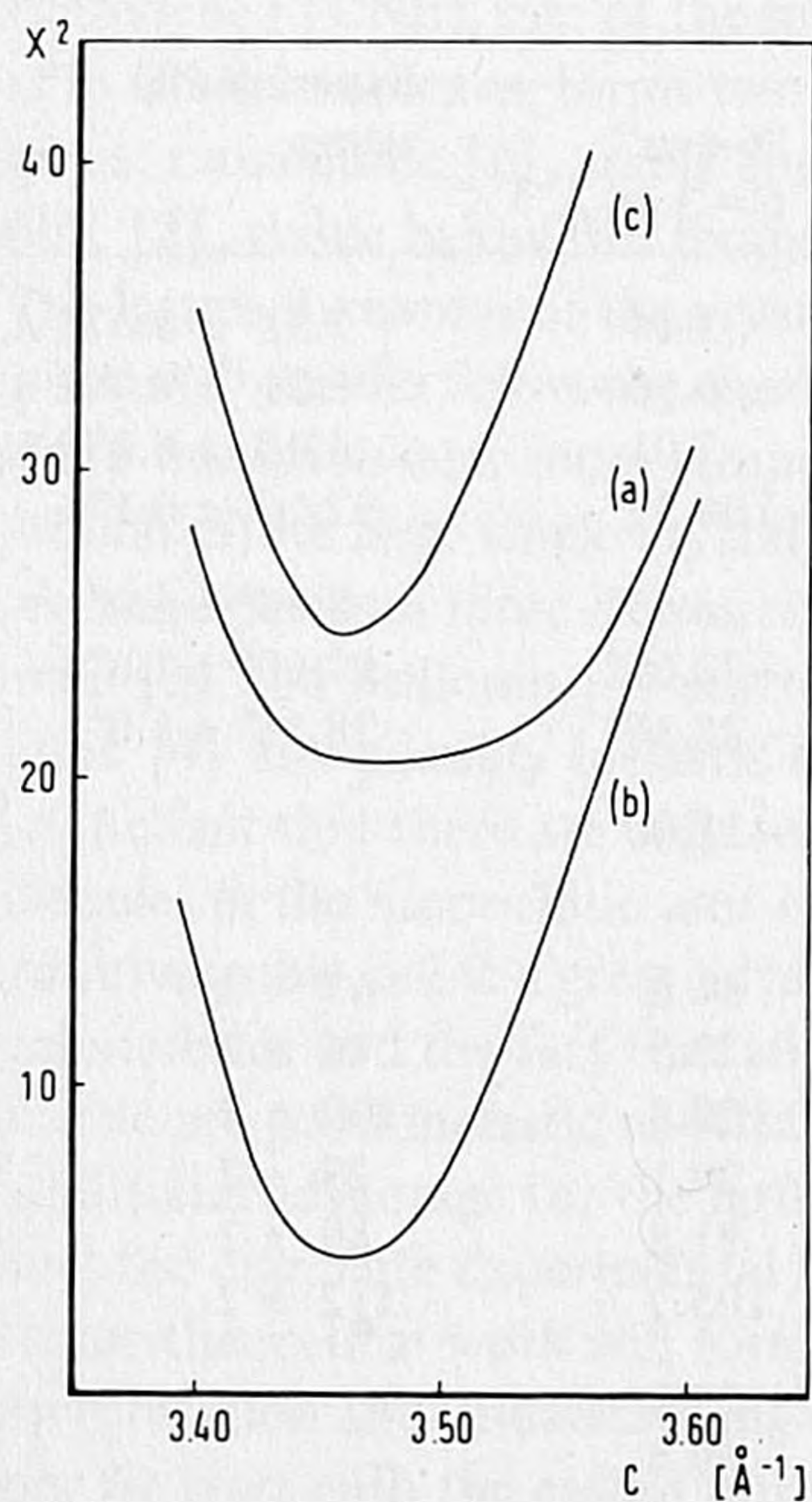


Fig. 1. Variation of  $\chi^2$  with the exponent  $C$  for monoclinic TCNE, as for structural parameters (curve a) and librational frequencies (curve b). The minimum of the total function (curve c) indicates the optimum value of the exponent  $C$ .

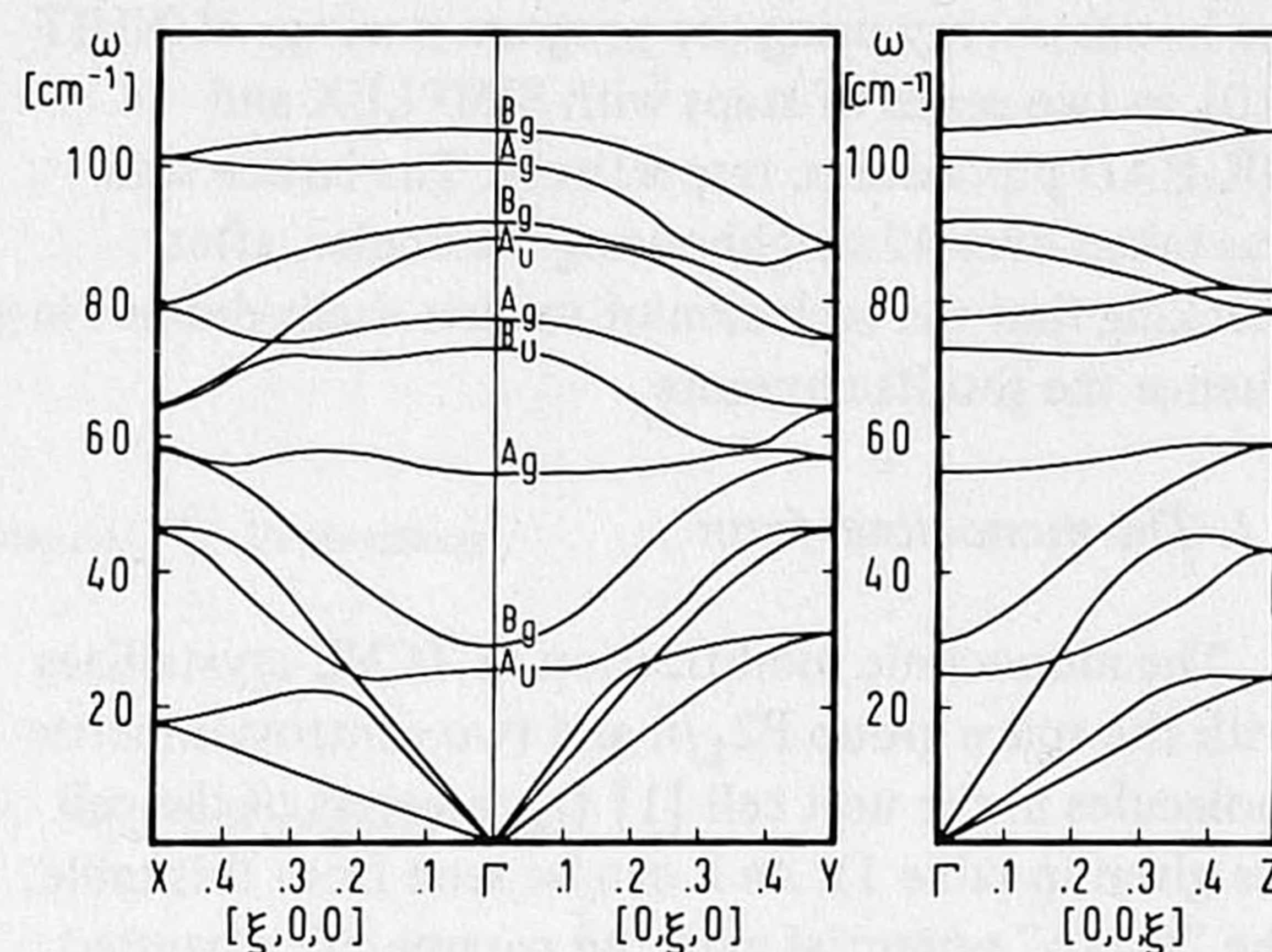


Fig. 2. Calculated phonon dispersion curves for monoclinic TCNE along the [100], [010] and [001] directions, using the parameter set from table 2.

ues derived directly from fits to ab initio calculations [8]. Both parameter sets yield good agreement for the static and dynamical properties of the monoclinic TCNE, the empirical set still performing somewhat better than the mixed empirical/ab initio set. Additionally, for comparison with the planned neutron experiment [5], fig. 2 shows the calculated phonon dispersion curves for three directions.

## 2.2. The cubic form

The cubic modification of TCNE crystallizes with the space group  $Im\bar{3}$ , six molecules in the unit cell with the edge  $9.736 \text{ \AA}$  [2]. The minimization of the

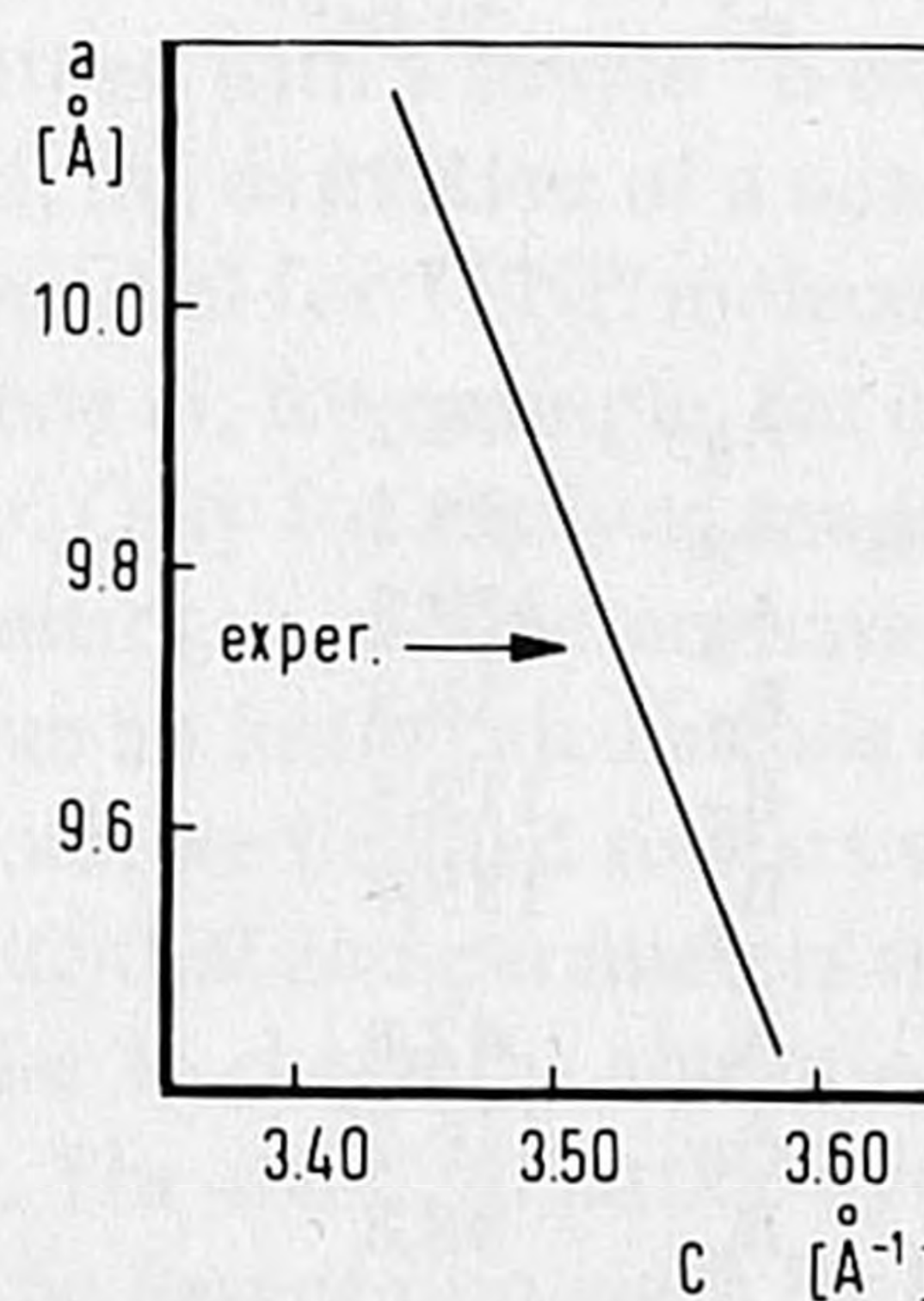


Fig. 3. Unit cell edge,  $a$ , of the cubic phase of TCNE plotted versus the exponent  $C$  (the arrow indicates the experimental value).



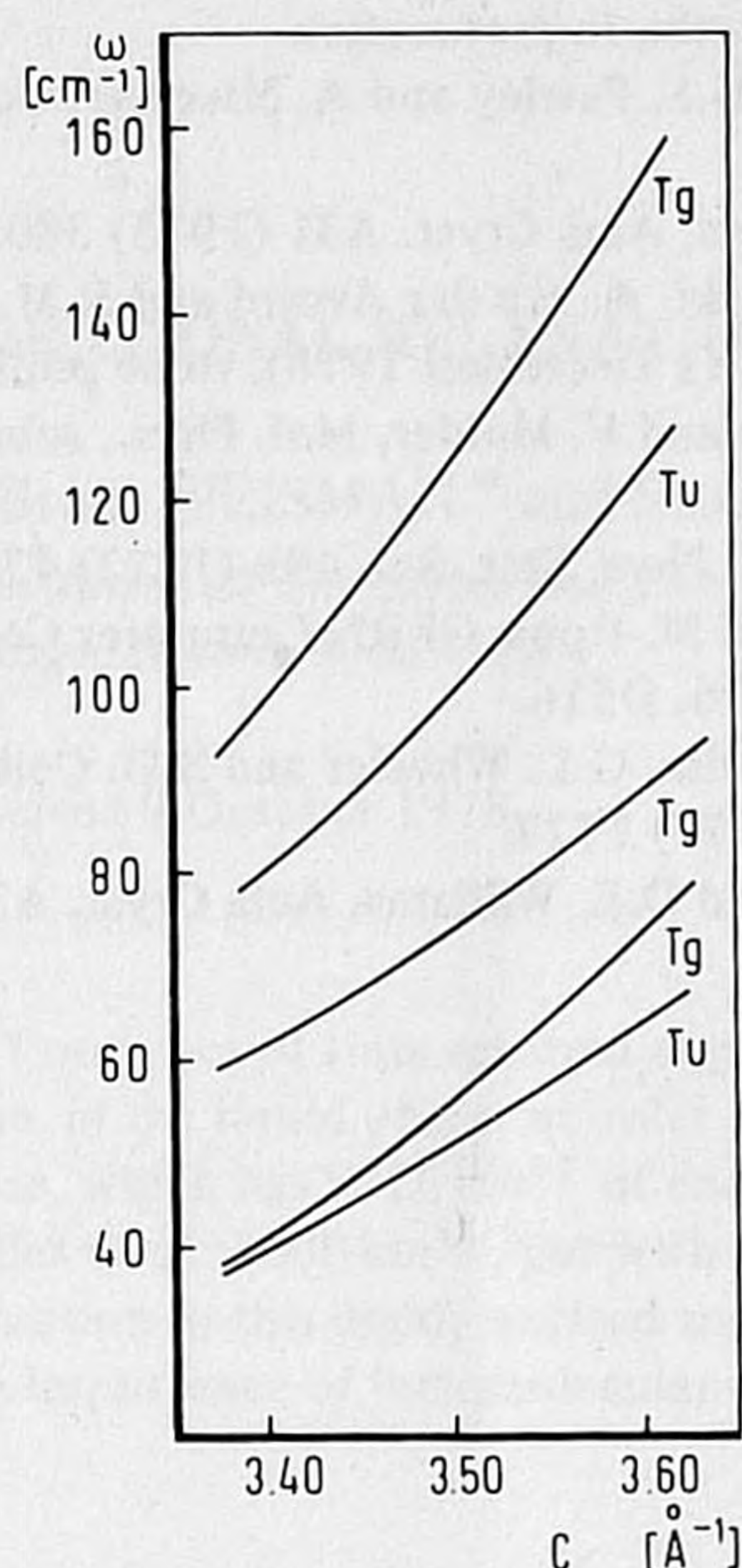


Fig. 4. Lattice mode frequencies at zero wave-vector for cubic TCNE plotted versus the exponent  $C$ .

crystal structure is very simple as there is only one parameter — the unit cell edge,  $a$ ; positions and orientations of the molecules are fixed by the space group symmetry. The parameter  $a$  appears to depend linearly on the exponent  $C$  (fig. 3) and the experimental value is reproduced for  $C = 3.52 \text{ Å}^{-1}$ , which is slightly larger than the value of  $3.46 \text{ Å}^{-1}$  for the monoclinic phase but still smaller than the usual empirical value  $3.60 \text{ Å}^{-1}$ . Experimental frequencies of lattice vibrations in this modification are not yet available, so we present the results of lattice dynamics calculations (for  $q = 0$  only) as a function of the exponent  $C$  (fig. 4). Comparison with future results from IR and Raman spectroscopy, allows one to read directly the best value of  $C$  from this figure.

### 3. Conclusions

From the present lattice dynamics calculations in comparison with experimental data for two crystal modifications of TCNE it appeared that a smaller exponent for the carbon and nitrogen contacts,  $C = 3.46 \text{ Å}^{-1}$ , improves the empirical "6-exp" atom—

Table 2

Set of parameters in the "6-exp" function,  $-Ar^{-6} + B \exp(-Cr)$  for crystals with cyano groups

Contact	$A$ (kcal/mole $\text{Å}^6$ )	$B$ (kcal/mole)	$C$ ( $\text{Å}^{-1}$ )
C...C	568	83630	3.46
C...N	374	11340	3.46
N...N	762	105600	3.46

atom potential proposed by Govers [6] for molecular crystals with cyano groups (see table 2). A similar conclusion related to the empirical parameter for the C...C contacts was recently drawn from a comparison with ab initio results for  $\text{C}_2\text{H}_4-\text{C}_2\text{H}_4$  interactions [7]. Concerning Govers' potential one may further observe that the  $A_{\text{C-N}}$  parameter is not the usual geometrical average of  $A_{\text{C-C}}$  and  $A_{\text{N-N}}$ . This must be a consequence of Govers fitting the experimental data without this constraint for  $A_{\text{C-N}}$ , in combination with the fact that the various fit parameters are highly correlated then. In several cases [7,8], the application of averaging constraints for hetero-atomic contacts, together with slight shifts in the homo-atomic contact parameters, yielded practically the same total dispersion interaction between the molecules. It is worth mentioning also that the total dispersion interaction calculated with Govers' parameters for various azabenzene molecules agrees rather closely with ab initio calculations [8]. On the other hand, the use of atom—atom parameters fitted to ab initio dispersion energies for the azabenzenes (parameter set IV of ref. [8]) yielded lattice dynamics results in reasonable agreement with experimental data for TCNE (the third column of table 1).

Furthermore, the present calculations support the concept of transferability of our atom—atom potential (table 2) between the different crystal modifications: the optimal exponents,  $C$ , for both phases are quite close, while the potential for the monoclinic phase (where more experimental information is available) also reproduces the structure of the cubic phase (with the same accuracy as the monoclinic phase). This transferability was not found for the different phases of *p*-dichlorobenzene [11], but it should be noted that in neither phase of TCNE extra-short atom—atom contacts occur.



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